Orbital Correlation Effects in Transition Metal Microclusters

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Orbital Correlation Effects in Transition Metal Microclusters

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Within the framework of a self-consistent tight-binding LDA+U approach established in the present work, it is argued that orbital correlation (OC) has crucial effects to very small transition metal microclusters (with number of atoms N typically less than 10) by leading to orbital polarized ground states. Numerical calculations on Fe, Co and Ni diatomic pairs have revealed that inclusion of OC changes magnetic properties fundamentally: the inter-atomic exchange couplings are at least one order smaller than the bulk values and change with respect to electron filling from antiferromagnetic (for Fe) to ferromagnetic (for Ni), and the magnetic easy axis is usually completely different after the OC effect is considered.

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I. Introduction

In recent years, transition metal (TM) microclusters have attracted considerable attention driven by both practical and fundamental interests[1]-[6]. Recent experimental developments have made it possible to generate, characterize, and study size-selected clusters in beams[1], and to form diverse nanometer-scale adatom structures at surfaces[2][3]. Experimental studies have inferred that the TM atoms generally possess enhanced magnetization and stronger magnetocrystalline anisotropy (MCA) energy compared to corresponding bulk values, and have shown that the magnetism develops from atom like to bulk like behaviors as the cluster size is increased[1].

Studies on TM microclusters provided both chances and challenges to theoretical researchers. Due to lacking of translation-invariant symmetry, first-principle calculations usually require much more computational efforts in such finite-size systems than bulk calculations, and require even more to study the MCA properties since the spin-orbit coupling (SOC) has further lowered the symmetry. Tight-binding (TB) model approach then becomes a powerful tool to analysis the magnetism including the MCA properties of TM microclusters, although usually TB approach can only catch the qualitative features rather than quantitative results. The first self-consistent TB calculation on the magnetism of TM microclusters was presented by Pastor, Dorantes-Dávila, and Bennemann about ten years ago[4], and since then, the same group has studied various magnetic properties of TM microclusters[5][6], including the MCA properties very recently by extending their model to incorporate the SOC term[6]. In the same spirit as other TB models on the magnetism of solids and films[7]-[10], the TB Hamiltonian proposed by Pastor *et al.* for microclusters includes usually a hopping term, a SOC term, and an electron-electron (*e-e*) interaction term in the following approximate form:

$$H_{ee}^{\mathrm{Spin}}=\sum_{im\bar{\sigma}}[Un^{i\bar{\sigma}}+(U-I)n^{i\sigma}]C_{im\sigma}^{+}C_{im\sigma}-E_{dc}^{\mathrm{Spin}}, \qquad (1)$$

where $n^{i\sigma}$ denotes the on-site spin density, U and I are Coulomb repulsion and exchange interaction, and $E_{dc}^{\mathrm{Spin}}=\frac{1}{2}\sum_{i\sigma}[Un^{i\sigma}n^{i\bar{\sigma}}+(U-I)n^{i\sigma}n^{i\sigma}]$ is a double-counting correction. Equation (1) is certainly a Hartree-Fock-like mean-field approximation adopting a Stoner exchange parameter I to split the up-spin and down-spin bands. Within this approximation, the ground state at the zero SOC limit is an orbital quenched (OQ) one with zero orbital moment. The introduction of the SOC induces a net orbital moment usually proportional to ξ, and an MCA energy usually proportional to ξ^2 in the systems with symmetry lower than cubic. By using this model, it is indeed shown that the magnetization in microclusters is enhanced with respect to corresponding bulk values[4][5], and the MCA energies can be considerably larger than those of thin films and solids[6], being consistent with experimental observations. The key point is that those surface atoms behave certainly different from the internal atoms due to lacking of neighbors so as to possess high magnetization and strong MCA energy.

However, despites of these successes, the limitation of this approach, as well as those for other systems, is clear—it only considers *spin* correlation but completely misses *orbital* correlation (OC)[4]-[10]. To be applicable, this rather generally adopted TB approach requires that the ground state has to be close to the OQ state. While this assumption seems to hold for the case of bulk TM systems, it is not generally guaranteed in arbitrary systems, especially in low-dimensional systems. For example, the ground state of a free atom should be a fully orbital polarized (OP) one according to Hund's second rule. In fact, it has been shown that the magnetic prop-

erties (including MCA) of TM linear chains can be completely changed by including the OC correction—although the conclusions of enhanced magnetization and stronger MCA energy remain unchanged, the sign of the MCA energy has been changed by the OC correction resulting in different magnetic easy axis[11]. Even in bulk transition metals where the ground states are certainly close to the OQ ones due to strong hopping, explicit inclusion of OC greatly enhances their orbital moments and prominently changes their MCA properties as shown by first-principles calculations of Trygg *et al.*[12][13] Thus, when the cluster's size decreases so that the effective hopping is weakened, whether the ground states are still close to the OQ states and whether approximation (1) is still applicable turns to be questionable in some cases.

The present work is devoted to clarifying the role of OC and examining the validity of approximation (1) in TB approaches for TM micorclusters, within a more general framework in which the OC effect is explicitly included. Through an approximate but rather general energy argument, we will show that the above assumption of the OQ ground state doesn't always hold, especially for very small clusters with number of atoms N typically less than 10. Then, by detailed numerical calculations for Fe, Co, and Ni diatomic pairs based on a self-consistent TB approach, we show that inclusion of OC does change qualitatively the magnetic properties of such systems. The present paper is organized as follows. The next section is devoted to the developments of the theoretical formalism of our self-consistent TB approach, then a general energy argument is presented in Sec. III to show whether the ground state is OQ one or OP one. The results for Fe, Co, Ni diatomic pair models are discussed thoroughly in Sec. IV, then the conclusions are summarized in the last section.

II. Theorectical Formalism

We adopt the general concept of the LDA+U method[14]-[16] to account for OC in our TB treatment. The appropriate Hamiltonian should contain the following main terms:

$$H=H_{\text{on}}+H_{\text{hop}}+H_{\text{soc}}+H_{ee}, \tag{2}$$

which describe the on-site electronic level ($H_{\text{on}}=\sum_{iL\sigma}e_{iL}C^{+}_{iL\sigma}C_{iL\sigma}$), the hopping interactions, the SOC term, and the *e-e* interactions. All of these terms are presented in second quantization forms by using the single-site atomic basis, $|iL\sigma\rangle$ in which i, $L\equiv\{lm\}$, and σ are the site, orbital, and spin indexes, which are defined in a *global*, but fixed, coordinates system. The hopping interaction is given by:

$$H_{\text{hop}}=\sum_{iLjL',\sigma} t_{ij}^{LL'}C^{+}_{iL\sigma}C_{jL'\sigma}. \tag{3}$$

The hopping matrix $t_{ij}^{LL'}$, which does not depend on the spin index, can easily be calculated according to Slater and Koster's scheme[17]. In the two-center approximation, only hopping parameters like $V_{dd\{\sigma,\pi,\delta\}}$, $V_{sd\sigma}$ etc. are required[17]. The SOC term is easily calculated as

$$H_{\text{soc}}=\xi\sum_{iLL'\sigma\sigma'}(\boldsymbol{S}_i\cdot\boldsymbol{L}_i)_{L\sigma,L'\sigma'}C^{+}_{iL\sigma}C_{iL'\sigma'}. \tag{4}$$

The *e-e* interaction, on the other hand, takes a different and more complicated form rather than eq. (1). Considering the original many-particle electron-electron interaction: $\mathscr{H}_{ee}=\frac{1}{2}\sum_{ij}(e^2/|\boldsymbol{r}_i-\boldsymbol{r}_j|)$, in the second quantization form, we obtain the following Hamiltonian:

$$H_{ee}=\frac{1}{2}\sum_i\sum_{\{L\},\sigma\sigma'}U_{LL_2L'L_3}C^{+}_{iL\sigma}C^{+}_{iL_2\sigma'}C_{iL_3\sigma'}C_{iL'\sigma}, \tag{5}$$

where

$$U_{LL_2L'L_3}=e^2\int d\boldsymbol{r}d\boldsymbol{r}'\frac{\phi^{*}_{L}(\boldsymbol{r})\phi^{*}_{L_2}(\boldsymbol{r}')\phi^{*}_{L_3}(\boldsymbol{r}')\phi^{*}_{L'}(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}. \tag{6}$$

Only the intra-atomic part of interactions are kept in eq. (5), since the electrons in TM systems are usually well-localized. Moreover, because 4s electrons are delocalized, we will only consider the interactions between 3d electrons as an approximation throughout the present work. The interacting parameters for 3d electrons $U_{mm_2m'm_3}$ are determined by two physical parameters: on-site Coulomb repulsion U and exchange J according to Refs. (14)-(16). It is noted that J is not the same as the Stoner exchange parameter I defined in eq. (1). Later we will discuss their relation.

Hamiltonain (5) is exact. However, it consists of four-operator interaction terms which can not be solved exactly. In a generalized Hartree-Fock (HF) approximation, we can decouple the four-operator terms into two-operator terms multiplied by a mean field term which is the expectation value of the remainder two-operator term. Considering all the possible pairings based on Wick's theory, we then have the following effective *e-e* interaction:

$$\begin{aligned}H_{ee}^{\text{eff}}\simeq&\sum_{i\{L\}\{\sigma\}}U_{LL_2L'L_3}[n^{i}_{L_2\sigma',L_3\sigma'}C^{+}_{iL\sigma}C_{iL'\sigma}\\&-n^{i}_{L\sigma,L_3\sigma'}C^{+}_{iL_2\sigma'}C_{iL'\sigma}]-E_{dc}\\=&\sum_i\sum_{\{L\sigma\},\{L'\sigma'\}}V^{i}_{L\sigma,L'\sigma'}C^{+}_{iL\sigma}C_{iL'\sigma'}-E_{dc},\end{aligned} \tag{7}$$

where

$$n^{i}_{L\sigma,L'\sigma'}=\langle C^{+}_{iL\sigma}C_{iL'\sigma'}\rangle \tag{8}$$

$$\begin{aligned}V^{i}_{L\sigma,L'\sigma'}=\sum_{L_2L_3}\{&[U_{LL_2L'L_3}\cdot n^{i}_{L_2\bar{\sigma},L_3\bar{\sigma}}\\&+(U_{LL_2L'L_3}-U_{LL_2L_3L'})n^{i}_{L_2\sigma,L_3\sigma}]\delta_{\sigma\sigma'}\\&-U_{LL_2L_3L'}\cdot n^{i}_{L_2\bar{\sigma},L_3\sigma}\delta_{\sigma\bar{\sigma}'}\},\end{aligned} \tag{9}$$

and

$$\begin{aligned}E_{dc}=\frac{1}{2}\sum_i\sum_{\{L\}}\sum_{\{\sigma\}}&U_{LL_2L'L_3}[n^{i}_{L\sigma_1,L'\sigma_1}\cdot n^{i}_{L_2\sigma_2,L_3\sigma_2}\\&-n^{i}_{L_2\sigma_2,L'\sigma_1}\cdot n^{i}_{L\sigma_1,L_3\sigma_2}]\end{aligned} \tag{10}$$

is a double-counting correction term. Under this generalized HF approximation, the total Hamiltonian (2) takes the following form:

$$H=\sum_{il\sigma,jL'\sigma'}H_{iL\sigma,jL'\sigma'}C^{+}_{iL\sigma}C_{jL'\sigma'}-E_{dc}, \tag{11}$$

where the Hamiltonian matrix is defined as

$$H_{iL\sigma,jL'\sigma'}=e_{il}\delta_{ij}\delta_{LL'}\delta_{\sigma\sigma'}+V^{i}_{L\sigma,L'\sigma'}\delta_{ij}+\xi(\boldsymbol{S}_i\cdot\boldsymbol{L}_i)_{L\sigma,L'\sigma'}\delta_{ij}+t_{ij}^{LL'}\delta_{\sigma\sigma'}. \quad (12)$$

Hamiltonian (11) can be diagonalized by the following transformation:

$$\begin{cases} C^{+}_{iL\sigma}=\sum_{\mathscr{K}} P^{*}_{iL\sigma,\mathscr{K}}\tilde{C}^{+}_{\mathscr{K}} \\ C_{jL'\sigma'}=\sum_{\mathscr{2}} P_{jL'\sigma',\mathscr{2}}\tilde{C}_{\mathscr{2}} \end{cases} \quad (13)$$

yielding

$$H=\sum_{\mathscr{K}} E_{\mathscr{K}}\tilde{C}^{+}_{\mathscr{K}}\tilde{C}_{\mathscr{K}}-E_{dc}, \quad (14)$$

where $\mathscr{K}$, $\mathscr{2}$ denote a set of quantum number like $\{iL\sigma\}$, $E_{\mathscr{K}}$ are the eigenvalues of the matrix, and $P_{iL\sigma,\mathscr{K}}$ are the corresponding eigenvectors. According to eq. (13), the on-site density matrix is now

$$n^{i}_{L\sigma,L'\sigma'}=\langle C^{+}_{iL\sigma}C_{iL'\sigma'}\rangle=\sum_{\mathscr{K}} P^{*}_{iL\sigma,\mathscr{K}}P_{iL'\sigma',\mathscr{K}}\Theta(E_f-E_{\mathscr{K}}) \quad (15)$$

in which E_f is the Fermi energy. All the matrix elements of the on-site density matrix should be self-consistently determined according to the above equation.

After the density matrix has been obtained, all the physical properties such as total energy, spin, orbital, and total magnetic moments can be fixed by the density matrix:

$$E=\frac{1}{N}[\sum_{\mathscr{K}} E_{\mathscr{K}}-E_{dc}] \quad (16)$$

$$\boldsymbol{M}^{S}_{i}=2\times\sum_{L\sigma,L'\sigma'} n^{i}_{L\sigma,L'\sigma'}(\boldsymbol{S}_i)_{\sigma\sigma'}\delta_{LL'} \quad (17)$$

$$\boldsymbol{M}^{L}_{i}=\sum_{L\sigma,L'\sigma'} n^{i}_{L\sigma,L'\sigma'}(\boldsymbol{L}_i)_{LL'}\delta_{\sigma\sigma'} \quad (18)$$

$$\boldsymbol{M}^{J}_{i}=\boldsymbol{M}^{L}_{i}+\boldsymbol{M}^{S}_{i}. \quad (19)$$

It should be noted that since both diagonal and off-diagonal terms of the density matrix in spin and orbital spaces are included, the present approach is invariant under rotations of both spin and orbital moments. All the physical quantities, for both collinear and non-collinear spin configurations, can be obtained in the same *global* and *fixed* coordinates systems, unlike the previous theories in which a local coordinates system for spin polarization should be introduced[7]-[10]. However, the price of such a rotation invariance is that a state with an assumed magnetized direction is not necessarily a self-consistent solution within the present approach. In order to get the angle-dependence of the energy, let us introduce an auxiliary field $\boldsymbol{h}_i$ to each site, with the direction of the field being what we want the magnetization to be aligned. This procedure corresponds to introduce the following interaction $-\sum_i \boldsymbol{h}_i\cdot\langle(2\boldsymbol{S}_i+\boldsymbol{L}_i)\rangle_{L\sigma,L'\sigma'}C^{+}_{iL\sigma}C_{iL'\sigma'}$, to our Hamiltonian (2). Under this auxiliary field, a state with total magnetic moment almost parallel to the field (although generally not exactly parallel to the field due to the crystal field effect) is easily found, then the energy of the present state, which is described the direction of the magnetic moment instead of that of the auxiliary field, can be obtained by deducting the interaction energy with the auxiliary field: $E=E(\{\boldsymbol{h}_i\})+\sum_i \boldsymbol{h}_i\cdot\boldsymbol{M}^{J}_{i}$. The validity of this method has been verified by examining some special points (say, along the crystal axis) in which self-consistently metastable states exist. The corresponding results turn to be rather insensitive to the strength of the auxiliary field $|\boldsymbol{h}_i|$ introduced and is the same as the zero-field limit within our numerical errors.

Thus, we have described the theoretical formalism of the self-consistent TB LDA + U approach for 3d systems. In numerical calculations throughout the present paper, the two center hopping integrals $V_{dd\{\sigma,\pi,\delta\}}$, $V_{ss\sigma}$, $V_{sd\sigma}$ etc. are taken from the canonical theory[19] with lattice constants assumed the same as bulk values, and the interacting parameters are set as: J, ξ=0.67, 0.073 eV which are believed to be reasonable estimations for 3d systems[6]. The parameter U is difficult to have an accurate estimation because it is sensitive to the environment which can give possible screening effect. The density functional estimation by Anisimov and Gunnarsson[15] for TM atoms is 5~6 eV, which is found to be rather good for insulators but is too strong for bulk metallic systems. With this in mind, we will first alter the value of U to see how our qualitative results depend on U in next section, then we will choose an appropriate value of U in section IV to study numerically some special examples.

The simplest example to test our approach is the isolated TM atom. With the model parameters mentioned above and setting U=5.74 eV which is certainly reasonable for isolated TM atoms, we have calculated the energies of multiples states for a Co atom and listed the results in **Table 1**. It is shown that the ground states of the Co atom is indeed consistent with Hund's rules. Moreover, it is found that the energy is unchanged under rotations of spin moments and orbital moments, showing the rotationally invariant nature of the present method.

III. Energy Arguments

Before carrying out self-consistently numerical calculations, it is helpful to first make a general argument to see whether the system should be in an OP state or in an

Table 1 Multiple states of an isolated Co atom, with energies arranged increasingly.

Spin-down electron occupations ($n^{i\downarrow}_{mm}$)					$M^{L}(\mu_B)$	Energy (eV)
−2	−1	0	1	2		
0.0	0.0	0.0	1.0	1.0	3.0	112.599
0.0	0.0	1.0	0.0	1.0	2.0	112.631
1.0	0.0	1.0	0.0	0.0	−2.0	112.778
1.0	1.0	0.0	0.0	0.0	−3.0	112.815
0.0	1.0	0.0	1.0	0.0	0.0	112.931
0.0	1.0	0.0	0.0	1.0	1.0	113.134
1.0	0.0	0.0	1.0	0.0	−1.0	113.200
0.0	0.0	1.0	1.0	0.0	1.0	113.364
0.0	1.0	1.0	0.0	0.0	−1.0	113.426
1.0	0.0	0.0	0.0	1.0	0.0	113.611

OQ one. Since it is 3d electrons that are mainly responsible for OC, in the present section, we only consider 3d electrons for simplicity. To estimate the dominant OC effect, let us simplify the effective *e-e* interaction energy based on the following two approximations. First, let us neglect the off-diagonal terms in both spin and orbital spaces, *i.e.* $n^i_{m\sigma,m'\sigma'}=n^{i\sigma}_m\delta_{mm'}$, then

$$\langle H_{ee}\rangle\simeq\frac{1}{2}\sum_{im_1m_2\sigma}[U_{m_1m_2}n^{i\bar\sigma}_{m_1}n^{i\sigma}_{m_2}+(U_{m_1m_2}-J_{m_1m_2})n^{i\sigma}_{m_1}n^{i\sigma}_{m_2}] \tag{20}$$

where

$$U_{m_1m_2}=U_{m_1m_2m_1m_2},\quad J_{m_1m_2}=U_{m_1m_2m_2m_1}. \tag{21}$$

Then, we average the interaction parameters by defining

$$U_{m_1m_2}=U\quad J_{m_1m_2}=J\quad (m\neq m_1), \tag{22}$$

the *e-e* interaction energy function is found to be

$$\begin{aligned}\langle H_{ee}\rangle&\simeq\frac{1}{2}U\sum_{i,m_1,m_2,\sigma}n^{i\bar\sigma}_{m_1}n^{i\sigma}_{m_2}+\frac{1}{2}(U-J)\sum_{i,m_1\neq m_2,\sigma}n^{i\sigma}_{m_1}n^{i\sigma}_{m_2}\\&=\frac{1}{2}\sum_i[Un^{i\bar\sigma}n^{i\sigma}+\frac{1}{2}(U-J)n^{i\sigma}n^{i\sigma}]\\&\quad-\frac{1}{2}(U-J)\sum_{i,m,\sigma}(n^{i\sigma}_m)^2.\end{aligned} \tag{23}$$

Based on the above two simplifications, the total energy is approximately calculated as

$$\begin{aligned}E&\simeq\langle|H_{\rm on}|\rangle+\langle|H_{\rm hop}|\rangle+\langle|H_{\rm soc}|\rangle+\langle|H^{\rm Spin}_{ee}|\rangle\\&\quad-\frac{1}{2}(U-J)\sum_{im\sigma}[(n^{i\sigma}_m)^2-(n^{i\sigma}/(2l+1))^2],\end{aligned} \tag{24}$$

where the Stoner exchange parameter I in $H^{\rm Spin}_{ee}$ should be interpreted by

$$I=\frac{2l}{2l+1}J+\frac{1}{2l+1}U. \tag{25}$$

The physics significance of the above equation is quite clear—among $2l+1$ orbitals, while the exchange interaction of electrons in different orbitals is J, it should be U for electrons in the same orbital.

Obviously, in addition to $\langle|H^{\rm Spin}_{ee}|\rangle$ which depends only on the *total spin*, the last term is an orbital correlation correction which is minimized when full orbital polarization arises: $n^{i\sigma}_m=0$ or 1. Thus, the ground state is a competing result of two aspects—the crystal field favoring an OQ state by lowering the hopping energy, and OC favoring an OP state by lowering the OC correction. Compared with eq. (24), it is shown that the widely adopted approximation (1) in previous TB method could be reasonable *only when* the OC correction is negligible compared to the hopping interaction. Unfortunately, this is not generally the case, especially in low dimensional systems.

As a semi-quantitative estimation, let us consider two limiting cases. The first one is the OQ state: $|{\rm OQ}\rangle$ (*i.e.*, the state calculated from (1)). The second one is a full OP state: $|{\rm OP}\rangle$ in which each atoms are in their atomic ground state determined by Hund's rules (*i.e.*, with largest spin and orbital polarization as listed in Table 1). Certainly both states are not eigenstates in general, however, comparison of their energy expectation values serves to show which might be nearer to the real physical ground state, although the actual ground state should possibly lie between this two limiting cases. An equality is used below to define approximately the phase boundary of the OQ-like state against an OP-like one. In the lowest order approximation, the total spin and thus the spin dependent energy $\langle|H^{\rm Spin}_{ee}|\rangle$ does not change, the expectation value of the hopping term in a full OP state is zero[18], and the SOC is much smaller than the other two terms (the hopping interactions and U). Thus, equating the two energies gives

$$\langle{\rm OQ}|H_{\rm hop}|{\rm OQ}\rangle-\frac{U_{\rm eff}}{2}\sum_{m\sigma}(n^\sigma_m)^2=-\frac{U_{\rm eff}}{2}n_d, \tag{26}$$

where $U_{\rm eff}=U-J$ and $\{n^\sigma_m\}$ are the output occupations in the OQ state.

According to the above arguments, we have calculated the critical values of $U_{\rm eff}$ when OP state is favorable, as the function of N with N being the number of atoms in Fe, Co, Ni clusters with both bcc-like and fcc-like structures. In order to take the possible hybridization effects into account, the number of d electrons are taken as 6, 7 (for Fe), 7, 8 (for Co), and 8, 9 (for Ni). The calculated critical values have been shown in **Fig. 1**, which are fitted to the following functions: $U^{\rm c}_{\rm eff}=U^{\infty}_{\rm eff}-A\cdot N^{-1/3}$, indicating the importance of the surface atoms. Although the exact value of $U_{\rm eff}$ is not known, in very small clusters ($N<10$) it is expected that the metallic screening effect should be limited so that the $U_{\rm eff}$ parameter should be close to theoretical estimation of 5 eV. It is clearly shown

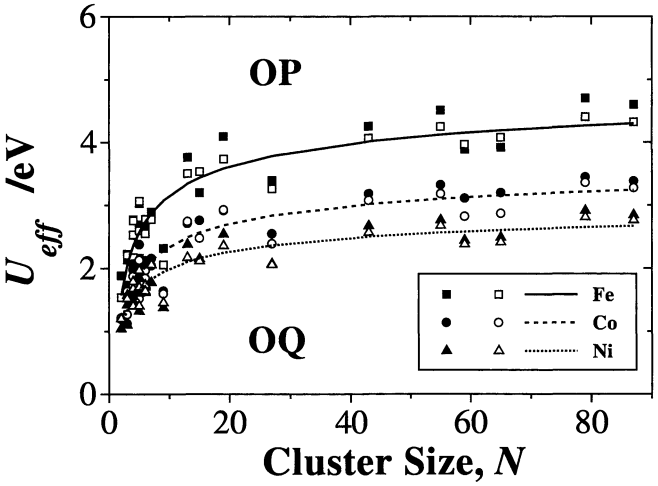

Fig. 1 Critical value of $U_{\rm eff}$, above which the OP state is preferred, as the functions of cluster's size N for Fe (n_d=6,7), Co (n_d=7,8) and Ni (n_d=8,9) clusters in both bcc and fcc structures. Solid symbols are for small n_d cases and open symbols are for large n_d cases, correspondingly. The lines represent functions $U^{\rm c}_{\rm eff}=U^{\infty}_{\rm eff}-AN^{-1/3}$ with parameters fitted by least-square technique. Fe: $U^{\infty}_{\rm eff}$=5.4 eV, A=4.8 eV, Co: $U^{\infty}_{\rm eff}$=4.1 eV, A=3.7 eV, Ni: $U^{\infty}_{\rm eff}$=3.3 eV, A=2.8 eV.

that the ground states of such very small clusters might be closer to the OP states instead of the OQ state. Such a tendency is even more drastic for Co and Ni systems where the crystal field is even weaker. As the cluster grows ($N>10$), on the one hand, the importance of the surface atoms decreases rapidly so that critical value U^c_{eff} increases, and on the other hand, the importance of the screening effect should also be enlarged leading to a smaller U_{eff}. Both effects make the ground states fo larger clusters closer to the OQ states. In the bulk limit, present consideration gives the critical values 5.4, 4.1, and 3.3 eV for Fe, Co, and Ni systems, respectively, being considerably larger than 2.0 eV for metallic systems. Thus, the ground states in that cases are indeed near the OQ states.

Thus, the general arguments have shown that the ground states of magnetic systems are not necessarily the OQ states as implied by previous theories without OC . Due to the competitions between the crystal field effect and the OC effect, the ground states in very small clusters should be the OP states. Later our numerical calculations will show that the fact that the ground state is orbital polarized may lead to completely different magnetic properties.

IV. Diatomic Pairs

Among various kinds of microclusters, diatomic pair is the most special one since all the basic features of a microcluster have been possessed by such a model despite of its simplicity. In order to show precisely the consequences of OC to the magnetic energies of small microclusters, we will study the Fe, Co, and Ni diatomic pairs in details.

4s electrons are also included in the following calculations to take the sd hybridization effect explicitly into account. Thus, the on-site energy differences between 3d and 4s levels, e_s-e_d, are also important model parameters. Let us estimate these parameters for Fe, Co, Ni according to their bulk magnetic properties. From eq. (24), it can be roughly estimated that the centres of up (down) 3d subband are

$$\begin{cases} C^{\uparrow}_d \simeq e_d + U\cdot n^b_d - I\cdot n^{\uparrow}_d = e_d + U\cdot n^b_d - I\cdot (n^b_d+\mu^b_d)/2 \\ C^{\downarrow}_d \simeq e_d + U\cdot n^b_d - I\cdot n^{\downarrow}_d = e_d + U\cdot n^b_d - I\cdot (n^b_d+\mu^b_d)/2, \end{cases} \quad (27)$$

where n^b_d and μ^b_d are the d-electron filling and magnetization. In bulk transition metals, it is known from experiments that the centres of 4s subbands are comparable with the down-spin 3d subbands. Thus, we can use

$$e_s \simeq C^{\downarrow}_d \quad (28)$$

to estimate roughly the values of e_s-e_d. Suppose U parameter is reduced to 2 eV in bulk systems due to metallic screening effect, $J=0.67$ eV so that $I=0.94$ eV, the values of e_s-e_d for Fe, Co, Ni are then estimated according to their 3d electron filling and magnetization as listed in **Table 2**. Although these can never be accurate estimations, we find that variations of e_s values around these estimations do not alter drastically magnetic properties. The reasons are quite straightforward. In such microclusters, due to lacking of efficiently metallic screening, the U parameter should approach the theoretical estimation of 5~6 eV, being appreciably higher than the metallic bulk value. Thus, the 3d subbands in such isolated systems would be much higher than the corresponding 4s subbands, so that a variation of e_s value in several eV's range should only have very limited influence to any magnetic properties in very small microclusters.

Table 2 e_s-e_d (in unit of eV).

Systems	n^b_d	μ^d_d	e_s-e_d
Fe	6.93	2.20	11.6
Co	7.87	1.65	12.8
Ni	8.97	0.67	14.0

With the above mentioned model parameters and $U=5.74$ eV, we have studied the angle dependence of the energy for Fe, Co, Ni diatomic pairs thoroughly. The angles $\{\theta_S, \phi_S\}$, $\{\theta_L, \phi_L\}$, $\{\theta_J, \phi_J\}$ are adopted to denote the polar angles of the spin, orbital and total magnetic moments.

First we study the case of collinear spin configurations. The energies per atom are calculated as functions of the magnetized direction θ_J in collinear configurations and are plotted in **Fig. 2** for Fe, Co, and Ni diatomic pairs.

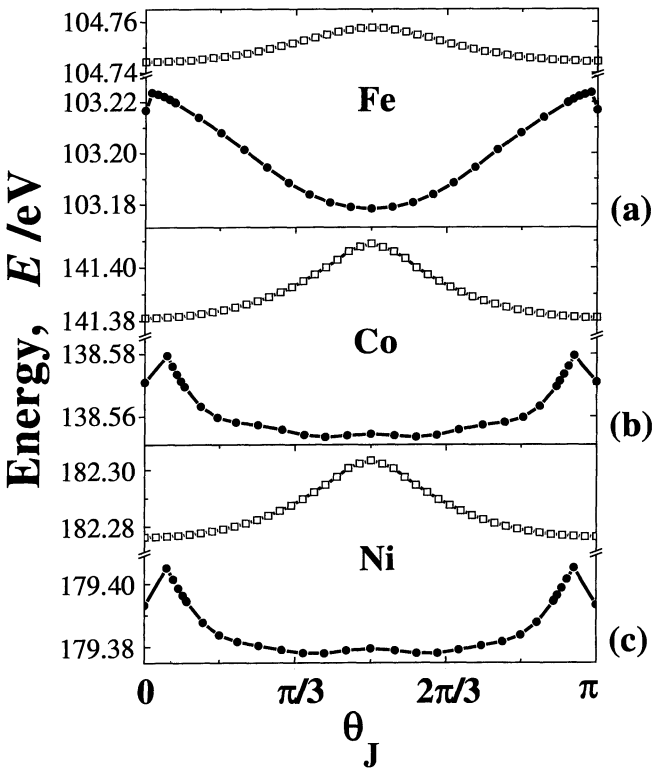

Fig. 2 Energies E as the functions of magnetization direction θ_J in collinear spin configurations for Fe, Co and Ni diatomic pairs, calculated with present (solid symbols) and previous approach (open symbols).

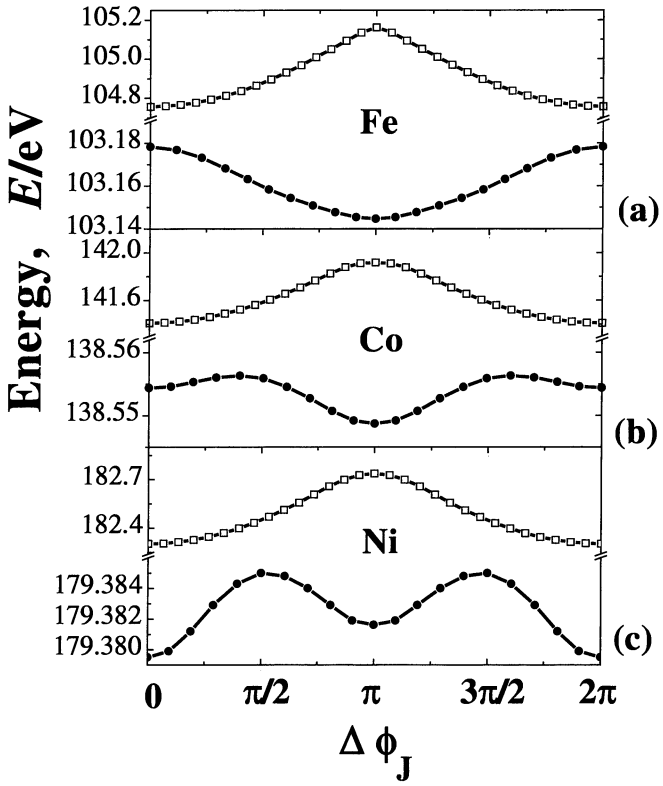

Fig. 3 Energies E as the functions of angle difference $\Delta\phi_J=\phi_J^1-\phi_J^2$ for Fe, Co and Ni diatomic pairs in the case of $\theta_J^1=\theta_J^2=\pi/2$, calculated with present (solid symbols) and previous approach (open symbols).

The corresponding results calculated by previous theory without OC have been plotted in the same figure for comparison. It is shown that for collinear spin configurations, it is expected that the easy-axis(plane) should be perpendicular to the chain axes while it is expected to be along the chain by previous theory without OC. It has been argued that such a discrepancy is caused by poor descriptions of the orbital polarization, which is unfortunately closely related the MCA energy, in previous theory due to missing of OC[11].

Next, we study the non-collinear configurations. In case of $\theta_J=\pi/2$, the energies per atom are plotted in **Fig. 3** as functions of $\Delta\phi_J=\phi_J^1-\phi_J^2$ for Fe, Co, and Ni systems. Again for comparison, results without OC are plotted in the same figure represented by open squares. It is shown that while previous theory predicts the magnetic atoms are ferromagnetically coupled with very strong exchange coupling ~ 0.4 eV, with OC considered, present theory predicts that the exchange coupling is much weaker and the sign of the exchange energy varies with respect to the number of d electrons. The exchange interaction strength decreases from Fe to Ni, and changes from antiferromagnetic type to ferromagnetic type.

V. Conclusions

To summarize, a self-consistent tight-binding LDA+U approach has been developed for transition-metal systems, in which the orbital correlation effects have been included automatically. General energy arguments have shown that, with commonly accepted value of Hubbard-U parameter, the ground states of those very small transition metal clusters (with number of atoms typically less than 10) should be orbital polarized states, instead of orbital quenched ones. Thus, the basic assumption in previous theory which only considers the spin correlation but misses the orbital effect, is incorrect for such systems. Self-consistent calculations on Fe, Co, and Ni diatomic pairs have shown that the orbital correlation effect changes fundamentally the magnetic properties of such systems. The inter-atomic exchange coupling is much weaker than that in the OQ state estimated by previous theory, and might be antiferromagnetic for Fe and Co. Although the magnetocrystalline anisotropy energy is also very strong similar to previous predictions, the magnetic easy axis, however, is usually different from previous prediction even in collinear spin configurations.

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(18) Full OP state is defined as $|OP\rangle=\Pi_i|G_i\rangle$, which means each atom is in its atomic ground state $|G_i\rangle$ determined by Hund's rules. In the lowest order approximation, we have $\langle OP|C^{+}_{im\sigma}C_{jm'\sigma'}|OP\rangle=\langle G_i|C^{+}_{im\sigma}|G_i\rangle\cdot\langle G_j|C_{jm'\sigma'}|G_j\rangle=0$. Thus, generally, we have $\langle OP|H_{\mathrm{hop}}|OP\rangle=0$.
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